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**UTILITY PATENT APPLICATION TRANSMITTAL**  
**(Large Entity)***(Only for new nonprovisional applications under 37 CFR 1.53(b))*Docket No.  
551512/062

Total Pages in this Submission

**TO THE ASSISTANT COMMISSIONER FOR PATENTS**Box Patent Application  
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

**A METHOD FOR SURFACE TREATMENT, ORNAMENTS AND ELECTRONIC DEVICES**

and invented by:

**Akira Uchiyama**If a **CONTINUATION APPLICATION**, check appropriate box and supply the requisite information:☐ Continuation ☒ Divisional ☐ Continuation-in-part (CIP) of prior application No.: 09/007,129

Which is a:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.:

Which is a:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.:

Enclosed are:

**Application Elements**

1. ☐ Filing fee as calculated and transmitted as described below
2. ☒ Specification having 51 pages and including the following:
  - a. ☒ Descriptive Title of the Invention
  - b. ☒ Cross References to Related Applications *(if applicable)*
  - c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*
  - d. ☐ Reference to Microfiche Appendix *(if applicable)*
  - e. ☒ Background of the Invention
  - f. ☒ Brief Summary of the Invention
  - g. ☒ Brief Description of the Drawings *(if drawings filed)*
  - h. ☒ Detailed Description
  - i. ☒ Claim(s) as Classified Below
  - j. ☒ Abstract of the Disclosure

# UTILITY PATENT APPLICATION TRANSMITTAL (Large Entity)

(Only for new nonprovisional applications under 37 CFR 1.53(b))

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Total Pages in this Submission

## Application Elements (Continued)

3. ☒ Drawing(s) (when necessary as prescribed by 35 USC 113)
- a. ☒ Formal                      Number of Sheets 3
- b. ☐ Informal                      Number of Sheets \_\_\_\_\_
4. ☒ Oath or Declaration
- a. ☐ Newly executed (original or copy)                      ☐ Unexecuted
- b. ☒ Copy from a prior application (37 CFR 1.63(d)) (for continuation/divisional application only)
- c. ☒ With Power of Attorney                      ☐ Without Power of Attorney
- d. ☐ DELETION OF INVENTOR(S)  
Signed statement attached deleting inventor(s) named in the prior application,  
see 37 C.F.R. 1.63(d)(2) and 1.33(b).
5. ☒ Incorporation By Reference (usable if Box 4b is checked)  
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6. ☐ Computer Program in Microfiche (Appendix)
7. ☐ Nucleotide and/or Amino Acid Sequence Submission (if applicable, all must be included)
- a. ☐ Paper Copy
- b. ☐ Computer Readable Copy (identical to computer copy)
- c. ☐ Statement Verifying Identical Paper and Computer Readable Copy

## Accompanying Application Parts

8. ☐ Assignment Papers (cover sheet & document(s))
9. ☐ 37 CFR 3.73(B) Statement (when there is an assignee)
10. ☐ English Translation Document (if applicable)
11. ☒ Information Disclosure Statement/PTO-1449                      ☐ Copies of IDS Citations
12. ☒ Preliminary Amendment
13. ☒ Acknowledgment postcard
14. ☒ Certificate of Mailing
- ☐ First Class                      ☒ Express Mail (Specify Label No.): EL 451 536 434 US

# UTILITY PATENT APPLICATION TRANSMITTAL (Large Entity)

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Docket No.  
551512/062

Total Pages in this Submission

## Accompanying Application Parts (Continued)

15. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed)

16. ☐ Additional Enclosures (please identify below):

## Fee Calculation and Transmittal

### CLAIMS AS FILED

For	#Filed	#Allowed	#Extra	Rate	Fee
Total Claims	24	- 20 =	4	x \$18.00	\$72.00
Indep. Claims	1	- 3 =	0	x \$78.00	\$0.00
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					\$0.00
BASIC FEE					\$760.00
OTHER FEE (specify purpose) _____					\$0.00
TOTAL FILING FEE					\$832.00

- ☐ A check in the amount of \_\_\_\_\_ to cover the filing fee is enclosed.
- ☒ The Commissioner is hereby authorized to charge and credit Deposit Account No. 19-4709 as described below. A duplicate copy of this sheet is enclosed.
- ☒ Charge the amount of \$832.00 as filing fee.
- ☒ Credit any overpayment.
- ☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
- ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Signature

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Dated: June 29, 2000

cc:

**CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)**

Applicant(s): Akira Uchiyama

Docket No.

551512/062

Serial No.

09/007,129

Filing Date

Herewith

Examiner

Group Art Unit

Invention: A Method For Surface Treatment, Ornaments and Electronic Devices

I hereby certify that this Divisional Application*(Identify type of correspondence)*

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Commissioner of Patents and Trademarks, Washington, D.C.

20231-0001 on June 29, 2000*(Date)*Lisa Jakob*(Typed or Printed Name of Person Mailing Correspondence)*  
*(Signature of Person Mailing Correspondence)*EL 451 536 434 US*("Express Mail" Mailing Label Number)***Note: Each paper must have its own certificate of mailing.**

Docket No.  
551512/062  
LR:LAJ

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants : Akira Uchiyama  
Serial No. : New Application  
For : New Divisional Application based on pending Application Serial No.  
09/007,129 filed on January 14, 1998, entitled A METHOD FOR  
SURFACE TREATMENT, ORNAMENTS AND ELECTRONIC  
DEVICES

June 29, 2000

**PRELIMINARY AMENDMENT TO THE ACCOMPANYING  
DIVISIONAL APPLICATION FILED UNDER 37 C.F.R. § 1.53(b)**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Before consideration of the above referenced divisional application, Applicants respectfully  
request the entry of the following amendments.

**IN THE SPECIFICATION**

At page 1, after the Title of the Invention and before "BACKGROUND OF THE INVENTION",  
please insert the following new paragraph:

**"Express Mail" Mailing Label**

Number: EL 451 536 434 US

Date of Deposit: June 29, 2000

I hereby certify that this paper or fee is being deposited with the  
United States Postal Service "Express Mail Post Office to Addressee"  
service under 37 C.F.R. 1.10 on the date indicated above and is  
addressed to: Assistant Commissioner for Patents, Washington, D.C.  
20231.

Name: Lisa Jakob

Signature: 

--This application is a divisional of Application Serial No. 09/007,129 filed on January 14, 1998.--.

**IN THE CLAIMS**

Please cancel claims 25-39.

**REMARKS**

This application is a divisional of U.S. Serial No. 09/007,129 filed on January 14, 1998. An Office Action was issued by the U.S. Patent and Trademark Office in connection with U.S. Serial No. 09/007,129 on March 23, 1999 and in a telephone response applicants elected to prosecute Group II claims 25-39, which is reflected in the Official Action mailed on July 8, 1999. Accordingly, U.S. Serial No. 09/007,129 is pending today and the subject divisional application is co-pending therewith for the purposes of 35 U.S.C. §120. Thus, the claims pending in the subject divisional application are claims 1-24.

The amendments to the specification and claims conform the subject application in light of a restriction requirement issued in the parent application. No new matter has been added. Accordingly, applicants respectfully request entry of this Preliminary Amendment.

Early and favorable action is requested.

Respectfully submitted,



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APPLICATION OF

AKIRA UCHIYAMA

FOR LETTERS PATENT OF THE UNITED STATES

FOR IMPROVEMENTS IN

A METHOD FOR SURFACE TREATMENT,  
ORNAMENTS AND ELECTRONIC DEVICES

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Name AKIRA UCHIYAMA  
Signature [Signature]

METHOD FOR SURFACE TREATMENT,  
ORNAMENTS AND ELECTRONIC DEVICES

BACKGROUND OF THE INVENTION

This invention relates generally to a method for surface treatment, and an ornament and electronic device, and in particular to applying a transparent protective layer on the surface of titanium or titanium alloys.

As described in Japanese Unexamined Utility Model Publication No. 56-74060, Japanese Unexamined Patent Publication No. 58-96869 and Japanese Unexamined Patent Publication No. 62-263977, methods for coating a metal surface, such as aluminum, with a rigid transparent coating film thereby adding corrosion resistant, abrasion resistant and impact resistant properties to the metal surface, are known in the art. The transparent coating film is generally composed of a variety of organic resins and inorganic substances.

In one surface coating technique, a transparent coating layer of rigid inorganic materials including aluminum oxide or aluminum silicon is conventionally coated on the surface of metal facing cases such as those used for watches and clocks.

In the case of wristwatches, machine works are generally applied to the surface of facing cases constructed from various kind of metals such as stainless steel, brass and other metals. Examples of such machine works are honing processing by blasting fine grains, nicking processing and mirror finishing by buff finishing or barrel finishing. When such machine works are used, surface adhesion substances such as oxide layers are very likely to



form on the surface of the facing cases, thus greatly diminishing the quality of appearance of the wristwatch.

Recently, titanium has been identified as a light and highly corrosion resistant material having a preventive effect for metal allergy. Often, titanium is used in combination with other metals where titanium is the main component thus forming a titanium alloy. Examples of metals that may be combined with titanium are Al, V, Mo, W, Fe, Co, Cr, Cu, Ag, Pt, Pd and Zn. The content of these metals is not especially limited as long as the metals do not alter the intrinsic properties of titanium.

Because titanium and titanium alloys oxidize easily, components constructed from these materials often have a titanium oxide layer (color change layer) formed on their surface. Formation of this oxide layer becomes evident when the machine works are applied to the component. The presence of an oxide layer can blacken the surface, which deteriorates the quality of appearance of the component and therefore should be avoided.

The facing case of a watch is produced by assembling facing members of watches such as a case body, rear cover, cover glass and the like. A bezel is provided around the periphery of the cover glass (water crystal) in some watches. At least one of the case body or bezel of the facing members of watches may be produced with titanium or titanium alloys.

The facing members of a wristwatch are often produced by press molding, casting, powder metallurgy, lost wax and metal injection molding (MIM) techniques using titanium or a titanium alloy as a starting material. An appropriate cutting process can

be applied to the facing member produced by press molding, if required.

Although titanium has advantages, problems can also exist when titanium is used for the facing case of a wristwatch. Although honing processing (honing finish) is the most frequently used machine works for finishing the surface of a facing case constructed from titanium, the surface of the titanium layer is easily damaged and oxidized when bombarded with glass beads during honing processing. This can blacken the surface. Also, because honing processing causes the surface to become uneven, the surface can be easily contaminated with fingerprints that are difficult to wipe off. In addition, when titanium is used for wristwatches, the wristwatches are more easily scratched because titanium has a Vickers hardness of only 150, which is less than the Vickers hardness of 200 for stainless steel (SUS).

Accordingly, it is desirable to provide a method and product which overcome drawbacks of the prior art.

#### SUMMARY OF THE INVENTION

Generally speaking, in accordance with the invention, a method for treating surfaces of titanium or titanium alloys which overcome drawbacks in the prior art is provided. The method includes the steps of applying a treatment for removing surface adhesion substances from the surface and then forming a transparent protective layer over the surface. The method of this invention can also be applied to titanium or titanium alloy surfaces that have been subjected to machine works, such as honing processing,

nicking processing or mirror finishing. By applying the method of this invention to a surface constructed from titanium or a titanium alloy, the surface acquires an improved appearance having a whitish and glossy finish. Also, the surface becomes more durable thus preventing scratches, abrasions and corrosion from diminishing the appearance of the surface.

Accordingly, it is an object of this invention to provide a method for improving the appearance of titanium or titanium alloy surfaces.

Another object of the invention is to provide a method for improving the appearance of titanium or titanium alloy surfaces to which machine works have been applied.

Further object of the invention is to provide a method for making titanium or titanium alloy surfaces more durable and scratch, fingerprint, corrosion and abrasion resistant.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specifications and drawings.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

### BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference is made to the following description taken in connection with the accompanying drawings, in which:

FIG. 1 is a cross sectional view of a facing member with an oxide layer formed on the surface;

FIG. 2 is a cross sectional view of the facing member of FIG. 1 after the oxide layer has been removed;

FIG. 3 is a cross sectional view of the facing member of FIG. 2 with a transparent protective layer formed on the surface;

FIG. 4 is a cross sectional view of a facing member with foreign substances adhering to the surface;

FIG. 5 is a cross sectional view of the facing member of FIG. 4 after the foreign substances have been removed; and

FIG. 6 is a cross sectional view of the facing member of FIG. 5 with a transparent protective layer formed on the surface.

### DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the FIGS. 1-3, there is shown a surface 10a of a facing member 10 of a watch after a machine work, such as honing processing, has been applied. An oxide layer (damaged oxide layer) 11, generated by the oxidation of titanium, is formed on surface 10a of facing member 10 constructed from titanium or a titanium alloy at the location where surface 10a suffers mechanical damage due to the application of machine works.

Because oxide layer 11 causes blackening of surface 10a of facing member, the appearance of the facing case of the watch is

impaired, even if a transparent protective layer 12, such as a glass coating, is later applied to surface 10a. This can result in an undesirable "wet" look and detract from the watch's ornamental appearance. Thus, the presence of oxide layer 11 will damage the marketability of a watch as a high-class timepiece.

In accordance with the present invention, the appearance of the facing case of a watch constructed from titanium or titanium alloys is improved by removing oxide layer 11 from surface 10a by applying, for example, chemical polishing, the result of which is shown in FIG. 2. Chemical polishing can be performed by placing surface 10a in contact with an etching solution. After oxide layer 11 is removed from surface 10a, a transparent protective layer 12 is formed on surface 10a of facing member, as shown in FIG. 3.

Preferably, transparent protective layer 12 contains a glass component. Using such a glass coating layer will create a "wetting" effect caused by the refractive indices of the glass, which gives surface 10a a whitish, high-gloss appearance. This coating layer will also prevent traces of fingerprints on surface 10a from spoiling the appearance of facing member 10.

Transparent protective layer 12 can be of any thickness. However, a thickness in the range of 0.2 to 15  $\mu\text{m}$  is preferred with a thickness in the range 0.8 to 5.0  $\mu\text{m}$  more preferable. A thickness in the preferred range yields transparent protective layer 12 having a sufficient protective effect as well as having good film quality with few faults.

If transparent protective layer 12 is too thick, cracks caused by an impact force on facing member 10 may develop because

the inner stress in transparent protective layer 12 is increased. If transparent protective layer 12 is too thin, its ability to prevent fingerprints from adhering to surface 10a and tiny scratches from appearing on surface 10a is diminished.

Transparent protective layer 12 can be of any hardness. However, a hardness in the range of 180 to 700, (expressed by a Vickers hardness defined in JIS Z 2244) is preferred, with a hardness in the range of 300 to 500 more preferable. This provides surface 10a with excellent abrasion and scratch resistance.

A method for surface treatment according to a preferred embodiment of the invention will now be described for purposes of illustration and is not intended to be construed as limiting.

#### 1. Elimination of surface adhesion substances

In this step, foreign materials such as oxide layer 11 and other contaminants (these are generally referred to as "surface adhesion substances") adhering to surface 10a of facing member 10 of a watch, especially on the portion of surface 10a subjected to machine works, are eliminated. By removing the surface adhesion substances from surface 10a, the inherent color of the substrate of facing member 10 is displayed even if surface 10a has previously exhibited a blackish color due to the oxidation of titanium. In this way, the quality of appearance of facing member 10 is improved because the degree of whiteness is enhanced and a high degree of glossiness is achieved.

Examples of treatments that can be used to remove the surface adhesion substances are (a) chemical polishing with an etching solution, (b) electropolishing, (c) washing with acids,

alkali or water and (d) a combination of chemical polishing, electropolishing and washing. These treatments will now be described in more detail.

(a) Chemical Polishing with Etching Solution

Chemical polishing with an etching solution is an effective method for removing surface adhesion substances, especially a layer of titanium oxide. Chemical polishing is performed by placing facing member 10 in contact with an etching solution, for example, by immersing facing member 10 in the etching solution.

There are no specific requirements with respect to the composition and temperature of the etching solution, or the length of time facing member 10 should be immersed in the etching solution. However, it is preferable that the etching solution comprises a mixed solution containing hydrofluoric acid (HF), nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). A mixed solution of HF and  $\text{HNO}_3$  may also be used, but the addition of  $\text{H}_2\text{SO}_4$  results in surface 10a that is whitish without exhibiting any roughness.

It is also preferable that the etching solution be an aqueous solution containing 1% to 10% vol of HF, 15% to 40% vol of  $\text{HNO}_3$  and 30% to 60% vol of  $\text{H}_2\text{SO}_4$ . By selecting such a composition range (the "optimum range"), the surface of facing member 10 can be polished to achieve a sufficient whiteness and glossiness within a comparatively short treatment time, and enable a high productivity polishing yield, without causing roughness to surface 10a.

When either one of HF and  $\text{HNO}_3$  is not present or contained in small amounts in the etching solution, etching will either not proceed substantially or will proceed slowly. For example, if the

content of HF is less than 1% vol or the content of  $\text{HNO}_3$  is less than 15% vol, little etching effect will be obtained and the treatment time can be prolonged.

When the content of HF is greater than 10% vol or the content of  $\text{HNO}_3$  is greater than 40% vol, surface roughness is likely to occur. Surface roughness is also likely to occur, resulting in a diminished etching effect, if the content of  $\text{H}_2\text{SO}_4$  is less than 30% vol or if the content  $\text{H}_2\text{SO}_4$  is greater than 60% vol.

Because surface roughness greatly affects facing member 10 to which a mirror finishing has been applied, it is more preferable to adjust the composition of the etching solution to 1% to 5% vol, 15% to 35% vol and 40% to 60% vol for HF,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , respectively.

In an exemplary embodiment, the etching solution is prepared by mixing 5% vol of commercially available 45% to 50% vol hydrofluoric acid, 45% vol of commercially available 60% to 70% vol nitric acid and 50% vol of commercially available 98% vol concentrated sulfuric acid. The composition of the etching solution in this embodiment is 2.25% to 2.5% vol of HF, 27% to 31.5% vol of  $\text{HNO}_3$  and 49% vol of  $\text{H}_2\text{SO}_4$  with the balance water, thereby satisfying the optimum range. Chemical etching is then performed by immersing facing member 10 in the etching solution for about 30 seconds.

As shown in Examples 8 to 14 in Table 1 below, a good appearance can be obtained by appropriately adjusting the immersion time in the etching solution or adjusting other conditions, such as the temperature of the etching solution, even if the composition of



the etching solution is out of the optimum range described above. Therefore, the composition of the etching solution used in accordance with this invention is not necessarily limited to the preferred optimum range.

The resulting quality of appearance of polished facing members 10 were evaluated by varying the composition of the etching solution and immersion times and subsequently washing facing members 10 with water. The results are listed in Table 1 below, together with the etching conditions. The substrate for the facing members used in this test was a sintered body formed by metal powder injection molding, the material being an alloy containing 6% wt of titanium and 1% wt of Al. Honing processing was applied on entire surface 10a of facing member 10. The etching temperature was 70°C in all cases.

Table 1

Example No	Composition ratio (% by volume)			Immersion time		
	HF	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	5 sec.	30 sec.	60 sec.
1	5.0	30.0	50.0	B	A	A
2	1.0	35.0	50.0	B	A	A
3	10.0	35.0	50.0	A	A	B
4	5.0	15.0	50.0	B	A	A
5	5.0	40.0	45.0	A	A	B
6	5.0	30.0	30.0	A	A	B
7	5.0	30.0	60.0	B	A	A
8	0.5	35.0	50.0	C	C	B
9	11.0	35.0	50.0	B	C	C
10	5.0	13.0	45.0	C	C	B
11	5.0	42.0	45.0	B	C	C
12	5.0	35.0	28.0	B	C	C
13	5.0	25.0	63.0	C	C	B
14	2.5	35.0	0	C	C	C
Comparative example 1	No etching treatment			E		

The quality of appearance of facing member 10 after etching was performed was classified into the following 5 ranks:

A: Very good appearance (a very high degree of whiteness)

B: Good appearance (a high degree of whiteness)

C: Normal appearance (a middle class of whiteness, slight roughness on the surface)

D: Rather bad appearance (blackish, roughness on the surface)

E: Bad appearance (evidently blackish, evident roughness on the surface)

Examples having an appearance rank of A or B are acceptable for all applications including those that require an especially high-grade of quality, while the examples having an appearance rank of C can be used for all applications except for those that require an especially high-grade of quality.

In Examples 1 to 7, etching solutions within the optimum range were used, while in Examples 8 to 14, etching solutions out of the optimum range were used. The products treated under the conditions of Examples 1 to 7 attained a superior quality of appearance than those treated under the conditions of Examples 8 to 14.

An excellent appearance was obtained in Examples 1, 2, 4 and 7 when the immersion time in the etching solution was a relatively long time of 30 seconds or 60 seconds, whereas an excellent appearance was obtained in Examples 3, 5 and 6 when the immersion time in the etching solution was a relatively short time of 5 seconds or 30 seconds.

In Example 8, a good appearance was obtained when the immersion time in the etching solution was 60 seconds because the content of HF was relatively small. On the other hand, when the content of HF was relatively large, such as in Example 9, a good

appearance was obtained when the immersion time in etching solution was only 5 seconds.

In Example 10, a good appearance was obtained when the immersion time in the etching solution was 60 seconds because the content of  $\text{HNO}_3$  was relatively small. On the other hand, when the content of  $\text{HNO}_3$  was relatively large, such as in Example 11, a good appearance was obtained when the immersion time in the etching solution was only 5 seconds.

In Example 12, a good appearance was obtained when the immersion time was only 5 seconds because the content of  $\text{H}_2\text{SO}_4$  was relatively small. On the other hand, when the content of  $\text{H}_2\text{SO}_4$  was relatively large, such as in Example 13, a good appearance was obtained when the immersion time was extended to 60 seconds.

In Example 14, the appearance was normal for an immersion time of up to 60 seconds because  $\text{H}_2\text{SO}_4$  was not added. However, a longer immersion time resulted in a good appearance (not shown).

In contrast, in Comparative Example 1, where no chemical polishing by etching was applied, the quality of appearance was bad.

The quality of appearance was also tested by varying the treatment time (immersion time) of facing member 10 subjected to honing processing, using a constant solution temperature and using an etching solution having the same composition as in Example 3 of Table 1. The results are listed in Table 2 below.

Table 2

Temp. of solution: 70°C

Treatment time (sec.)							
5	10	20	30	40	50	60	70
A	A	A	A	A	A	B	B

The quality of appearance was also tested by varying the solution temperature in which facing member 10 subjected to honing processing was immersed, and maintaining constant treatment time (immersion time) using an etching solution having the same composition as in Example 3 of Table 1. The results are listed in Table 3 below.

The methods used for evaluating the quality of appearance in Table 2 and Table 3 were the same as those used in Table 1.

Table 3

Treatment time: 30 sec.

Temp. of solution (°C)							
25	30	40	50	60	70	75	80
B	A	A	A	A	A	A	B

As shown in Table 2, an excellent quality of appearance was obtained at an etching solution temperature of 70°C and an immersion time of 5 to 50 seconds, with a gradual tendency to cause surface roughening when the treatment time was 70 seconds or longer. Accordingly, the preferable treatment time is 5 to 50 seconds. However, a treatment time of 5 to 30 seconds is more preferable because it yields better surface smoothness and improved productivity.

Although an excellent quality of appearance was obtained for a treatment time of 30 seconds at a temperature range of 30°C to 75°C, as shown in Table 3, the whiteness slightly decreased when the solution temperature was lowered to 25°C. Also, the etching effect was so enhanced when the temperature was raised to 80°C that there was a tendency to exhibit a slight surface roughness. Based on these observations, the preferable solution temperature range is 30°C to 75°C. However, a more preferable solution temperature range is 30°C to 60°C, because it yields a better surface appearance and improves safety by operating in a lower temperature range.

(b) Electropolishing

Electropolishing can also be used to remove surface adhesion substances from surface 10a of facing member 10 of watches constructed from titanium or titanium alloys. Electropolishing is performed by dissolving (anode dissolution) facing member 10 in an electrolyte solution using facing member 10 as an anode. Electropolishing is described hereinafter referring to FIGS. 4-6.

A plurality of foreign substances 13, other than the substrate metals of facing member 10, adhere to surface 10a on which machine works were applied. Foreign substances 13 bombarded into surface 10a are especially present in the case when facing member 10 is subjected to honing processing.

If transparent protective layer 12, such as a coating glass layer, is formed on surface 10a without first removing from surface 10a, foreign substances 13, the adhesive property and durability of transparent protective layer 12 will be decreased.

To overcome this problem, in accordance with the present invention, transparent protective layer 12 is formed on surface 10a after foreign substances 13 have been removed by applying electropolishing, the results of which are shown in FIG. 5. If oxide layer 11 was formed on surface 10a, electropolishing can be used to remove oxide layer 11 together with foreign substances 13.

According to the method described above, the film quality and adhesive property of transparent protective layer 12 is improved by removing foreign materials 13 from surface 10a, thereby making surface 10a uniform and substantially smooth. Thus, a transparent protective layer that is highly durable will be formed, possessing excellent fingerprint adhesion prevention and scratch resistant properties, as shown in FIG. 6.

Although the composition of the electrolyte solution, temperature, electric current density and treatment time are not limited to any particular values to provide the benefits under the present invention, preferable values for these conditions will be described below.

It is preferable that the composition of the electrolyte solution contain  $H_3PO_4$  (phosphoric acid). Electrolyte solution containing  $H_3PO_4$  is preferable for the electrolysis treatment of titanium or titanium alloys because it yields especially good surface properties.

The preferable concentration of the electrolyte solution is 8% to 12% vol. If the concentration of  $H_3PO_4$  is too low, the polishing strength is lowered and foreign substances 13 are not fully eliminated within a short treatment time. If the

concentration of  $H_3PO_4$  is too high, polishing strength is so enhanced that the color of facing member of watches 10 may be easily changed.

Although the pH of the electrolyte solution is not limited to a particular value, the preferable pH range is usually 1.0 to 1.2, with a pH range of 1.05 to 1.1 being more preferable.

The temperature of the electrolyte solution is not limited to a particular value, but is preferably in the range of 25°C to 30°C.

Electrolysis treatment time is not limited to a particular value, but is best determined based on the composition of the electrolyte solution and the electric current density used. To increase productivity, a treatment time of 3 seconds to 2 minutes is preferred, with a treatment time in the range of 5 seconds to 1 minute more preferred. If the electrolysis time is too short, electropolishing will be insufficient to yield the desired effect. On the other hand, even if electrolysis treatment time is made longer than the preferable treatment time, polishing will not be improved and a loss of productivity results.

The anode electric current density in electropolishing is not limited to a particular value, but a current density in the range of 0.5 to 10 amps per square centimeter ( $a/cm^2$ ) is preferable and a current density in the range of 1 to 5  $a/cm^2$  is more preferable. By using a current density in the preferred range, electropolishing will be rapidly performed and produce surface 10a with high a degree of whiteness and quality.



If the anode current density is too low, sufficient electropolishing cannot be achieved in a short treatment time. If the anode the current density is too high, the color of surface 10a of facing member 10 is often changed, (e.g. turns yellow), reducing whiteness, especially if the treatment time is prolonged.

It should be noted that treatment conditions such as the composition of the electrolyte solution, the pH and the electric current density are not limited to the conditions described above.

The testing procedures used to evaluate electropolishing and the results obtained will now be described.

Facing members 10 used in this test were produced via press processing and cutting processing with a honing processing applied to entire surface 10a. The composition of the metal substrate of facing member 10 that was used was pure Ti.

After subjecting facing member 10 to an alkaline degreasing and acid neutralization treatment, in that order, electropolishing was applied to facing member 10 by varying the anode electric current density and the electrolysis treatment time and using two types of electrolyte solutions followed by washing with warm water (70°C). The quality in appearance of facing member 10 was then evaluated. The composition of the electrolyte solution and the other electrolysis conditions are listed in Table 4 below and the results are shown in Table 5 below.

Table 4

Table 4 Electrolysis condition	Type 1	Type 2
Composition of electrolyte solution	Phosphoric acid ( $H_3PO_4$ ) : 11 vol% water : balance	Phosphoric acid ( $H_3PO_4$ ) : 8 vol% water : balance
Specific gravity of electrolyte solution	1.07	1.08
Temperature of electrolyte solution	30 °C	25 °C
Heating method for electrolyte solution	Quartz-sheathed electric heater	Quartz-sheathed electric heater
Stirring of electrolyte solution	Yes	No
Cathode material	Stainless steel	stainless steel

Table 5

Example No	Electrolysis condition	Anode current density ( $A/cm^2$ )	Electrolysis time					
			5 sec	15 sec	30 sec	60 sec	120 sec	130 sec
15	Type 1	0.5	B	A	A	A	A	A
16	Type 1	1.0	B	A	A	A	A	A
17	Type 1	2.0	A	A	A	A	A	A
18	Type 1	3.5	A	A	A	A	A	A
19	Type 1	5.0	A	A	A	A	A	B
20	Type 1	7.0	A	A	A	A	B	B
21	Type 1	10.0	A	A	A	A	B	C
22	Type 2	1.5	B	A	A	A	A	A
23	Type 2	2.5	A	A	A	A	A	A
24	Type 2	4.0	A	A	A	A	A	A
25	Type 2	5.0	A	A	A	A	A	A
26	Type 2	7.0	A	A	A	A	A	A
27	Type 2	10.0	A	A	A	A	A	B
28	Type 2	12.0	A	A	A	A	B	C
Comparative example 2	No electropolishing		E					

The quality of appearance after electropolishing was classified into the following 5 ranks as shown in Table 5:

A: Very good appearance (a very high degree of whiteness)

B: Good appearance (a high degree of whiteness)

C: Normal appearance (a middle class of whiteness, slight color change to yellow)

D: Rather bad appearance (color change to yellow or a little foreign substances remain)

E: Bad appearance (color change to yellow evident, foreign substances remain )

Examples having an appearance rank of A or B are easily used for all applications including those that require an especially high-grade of quality, while the examples having an appearance rank C can be used for all applications except for those that require an especially high grade of quality.

In Examples 15 to 28, all products achieved at least a good quality in appearance. Of these Examples, the ones in which anodic electric current density and electrolysis treatment time were made optimum, yielded an excellent quality of appearance.

When electric current density was relatively low (Examples 15 and 22), a good quality of appearance was obtained by increasing the concentration of phosphoric acid or slightly lengthening treatment time.

When electric current density was relatively high, e.g. Examples 20, 21, 26, 27 and 28, a good quality of appearance was obtained by decreasing the concentration of phosphoric acid or slightly shortening the electrolysis treatment time.

In contrast, the quality of appearance was bad in Comparative Example 2 where electropolishing was not applied.

(c) Washing Treatments

Washing treatment methods include acid washing, alkaline washing (including alkaline degreasing and neutralization with an acid), water washing, warm water washing, washing with organic solvents such as alcohol and oil washing. One of these methods or an appropriate combination of two or more of these method can be used. The inclusion of a washing step makes it easier to remove surface adhesion substances, especially surface contaminants and foreign materials having a weak adhering strength.

An acid solution that can be used for the acid washing method is, for example, 3% to 5% of sulfuric acid while the alkaline solution that can be properly used for the alkaline washing method is, for example, 3.5% to 5% of Deepsol 41C (made by Deepsol Co.) a mild alkaline solution.

The washing procedure may be of any type including shower washing, jet washing, ultrasonic washing, precision washing or simply immersing in a washing solution or immersing in washing solution while stirring the solution.

The temperature of the washing solution is not limited to a particular value and any temperature in the range of room temperature to 100°C can be used.

(d) Combination of Chemical Polishing, Electropolishing and Washing

The treatments described above in sections (a) to (c) can be used in any combination and in any order. For example, washing may

applied after chemical polishing or electropolishing to improve the appearance of surface 10a and make it cleaner. By combining these different treatment methods, the appearance of surface 10a can be delicately adjusted, thereby improving the adhesive property of transparent protective layer 12, as described hereinafter.

## 2. Formation of Transparent Protective Layer

After removing surface adhesion substances, as described above, transparent protective layer 12 was formed on surface 10a of facing member 10, the results of which are shown in FIG. 3 and FIG. 6.

Transparent protective layer 12 can be constructed, for example, from a glass coating layer. One method of forming the layer in accordance with the invention will now be described.

A glass coating liquid can be applied to surface 10a of facing member of watches 10 by, for example, a coating method followed by drying, so that a transparent glass coating layer is formed on surface 10a. A suitable glass coating liquid may be obtained by dissolving and heating an alkali silicate as a main component, together with fine granular silica (An example is the transparent glass coating agent made by Okuno Seiyaku Kogyo Co., trade name CRM Coat 100).

The glass coating liquid (an original liquid) is produced by dissolving 100 parts by weight (as converted to solid fraction) of an alkali silicate such as sodium silicate or potassium silicate and 5 to 100 parts by weight of fine granular silica having a mean grain diameter of 40  $\mu\text{m}$  and preferably heating the combination to a

temperature in the range of 50°C to 100°C, and more preferably, to a temperature in the range of at 80°C to 100°C, for about 1 to 2 hours to allow the fine granular silica to dissolve (disperse) into the alkali silicate.

Water may be added at an upper limit of 600 parts by weight against 100 parts by weight of the total solid fraction described above, which makes dissolution easy and rapid.

While the inorganic transparent glass coating liquid can be used as an original liquid or by diluting it with a diluting solvent, it is preferable to dilute it with a diluting solvent. This not only enhances the workability of the coating process but also improves the film quality of transparent protective layer 12, especially its hardness and corrosion resistance.

The ratio of the glass coating liquid to the diluting solvent is preferably selected depending on the type of machine works applied to facing member 10, e.g. honing processing, nicking processing or mirror finishing. Making the appropriate selection will result in improved color tones of facing member 10, including the degree of whiteness and glossiness, while maintaining the corrosion resistant, abrasion resistant and scratch resistant properties of transparent protective layer 12 at a high level.

The preferable dilution ratio, based on the type of the machine works used, will now be described. The preferable range for the viscosity of the glass coating liquid which proportional to the dilution ratio will also be described.

- Honing Processing

The preferable dilution ratio is 85% or less but a ratio of 30% to 70% is more preferable. For example, the dilution ratio can be adjusted to 70%, a water : original liquid (volume ratio) of 70 : 30, by adding water to the original liquid. The viscosity of the diluted solution is preferably in the range of 150 cps (25°C) or more, with a viscosity in the range of 200 to 500 cps (25°C) even more preferable.

- Nicking Processing

The preferable dilution ratio and viscosity for nicking processing is substantially identical to that for honing processing.

- Mirror Finishing

The preferable dilution ratio is in the range of 50% to 98% but a ratio of 90% to 98% is more preferable. For example, the dilution ratio can be adjusted to 95%, a water : original liquid (volume ratio) of 95 : 5, by adding water to the original liquid. The viscosity of the diluted solution is preferably in the range of 150 to 400 cps (25°C), with a viscosity in the range of 150 to 250 (25°C) being more preferable.

By using a dilution ratio that results in a viscosity in the preferred range, corrosion, abrasion and scratch resistance is improved. If, however, the dilution ratio is too high (the viscosity is too low), the corrosion, scratch and abrasion resistance properties of transparent protective layer 12 obtained

from the glass coating liquid may be decreased. If the dilution ratio is too low (the viscosity is too high), the degree of whiteness or glossiness is decreased especially in members subjected to mirror finishing.

When transparent protective layer 12 is composed of a material other than glass, for example, an organic coating film, organic diluting solvents such as alcohols, benzene and toluene are used. These organic solvents can be used by mixing with water.

The glass coating liquid can be applied using a variety of coating methods including immersion (dipping), spraying, roll coating and coating with a brush.

The coating liquid applied to surface 10a is then dried. Drying conditions are not in any way limited, but it is preferable that drying be carried out at a temperature in the range of room temperature to 250°C for 1 to 20 minutes, with the temperature range of 150°C to 230°C for 5 to 15 minutes being more preferable.

Drying may be performed two or more times under the same or different drying conditions. When drying is performed two or more times under different conditions (i.e. at least one parameter, e.g.; drying temperature or drying time (drying speed), is varied), the film qualities (especially denseness, homogeneity and uniformity of thickness) and adhesive property of transparent protective layer 12 is improved.

The coating and drying cycle may be repeated several times. For example, a glass coating liquid can be sprayed on the front portion of surface 10a of a wristwatch case using a spray gun followed by a temporary drying at 150°C for 10 minutes. Then, the



same glass coating liquid can be sprayed on the rear portion of surface 10a (inner surface) followed by a temporary drying at 150°C for 10 minutes. Next, the coated case is subjected to a final drying at 180°C for 10 minutes using a drying fan and ventilation fan resulting in transparent protective layer 12 made from a glass layer being formed. Transparent protective layer 12 using this procedure has sufficient hardness resulting in good corrosion resistant, abrasion resistant, scratch resistant, impact resistant, fingerprint adhesion preventive and adhesive properties.

To improve the corrosion resistance, abrasion resistance and scratch resistance properties provided by transparent protective layer 12, a plurality of glass coating liquid (coating liquid) application steps may be performed.

The testing procedures used to evaluate different coating liquids and the results obtained will now be described.

A concentrate of an original liquid used for a glass coating liquid was obtained by dissolving and heating 100 parts by weight (as converted to a solid fraction) of sodium silicate together with 50 parts by weight of fine granular silica having a mean grain diameter of 30  $\mu\text{m}$  at 85°C followed by stirring the solution for about 1 hour to dissolve (disperse) the fine granular silica into alkali silicate. The original liquid was then diluted with water in varying ratios to prepare glass coating solutions with a different dilution ratios and viscosities (25), as shown in Table 6 below.

Each glass coating solution was applied to surface 10a of different facing members 10 of watches after immersion in etching

solution for 30 seconds. The different glass coatings were applied to surface 10a using the spray method. Then, a temporary drying step at 160°C for 8 minutes and a final drying step at 185°C for 10 minutes was applied resulting in the formation of transparent protective layers 12 having thicknesses (mean value) as shown in Table 6.

The resulting quality of appearance, Vickers hardness, fingerprint adhesion resistance, scratch resistance and adhesion property of transparent protective layer 12 was evaluated. The results are listed in .

Table 6

Example No	Dilution ratio	Viscosity of coating solution (cps)	Thickness of transparent protective layer ( $\mu\text{m}$ )	Appearance			Hv	Fingerprint adhesion resistance	Abrasion resistance				Adhesive property of transparent protective layer
				H	S	M			Test 1	Test 2	Test 3	Test 4	
29	10%	500	10.0	A	A	C	600	○	○	○	○	○	○
30	30%	450	5.0	A	A	C	500	○	○	○	○	○	○
31	50%	400	4.0	A	A	B	350	○	○	○	○	○	○
32	70%	300	2.0	A	A	B~A	250	○	○	○	○	○	○
33	80%	250	0.8	A	A	A	180	○	○	○	○	○	○
34	90%	200	1.0	A	A	A	200	○	○	○	○	○	○
35	95%	200	1.0	A	A	A	200	○	○	○	○	○	○~○
Comparative example 3	Transparent protective layer is not formed.			—	—	—	—	X	△	△	△	X	—
Comparative example 4	80%	250	2.0	E	D~E	E	250	○	○	○	○	○	○

The reference characters H, S and M in the Appearance column in Table 6 correspond to honing processing, nicking processing and mirror finishing, respectively.

The quality in appearance was visually evaluated and classified into the following five categories:

A: Very good appearance (a very high degree of whiteness and glossiness)

B: Good appearance (a high degree of whiteness and glossiness)

C: Normal appearance (a middle class of whiteness and glossiness)

D: Rather bad appearance (a little whiteness and glossiness)

E: Bad appearance (no whiteness and glossiness)

Examples having an appearance rank A or B are easily used for all applications including those that require an especially high-grade of quality, while the examples having an appearance rank of C can be used for all applications except for those that require an especially high grade of quality.

Fingerprint adhesion resistance was evaluated based on the degree of fingerprint adhesion caused by a light touch of fingers on surface 10a to which machine works H and M were applied, and the results were classified into the following 4 ranks:

- ⊙ no adhesion of fingerprint
- insignificant adhesion of fingerprint
- △ some adhesion of fingerprint
- X obvious adhesion of fingerprint

Scratch resistance was evaluated for surfaces 10a to which mechanical work H was applied. In Test 1, surface 10a was scratched  $1.5 \times 10^4$  times with a sheet of cowhide under an applied pressure of 500 g/cm<sup>2</sup>. In Test 2, scratching was performed with a piece of Aluminum (Al). In Test 3, scratching was performed with a piece of Brass (Bs). In Test 4, scratching was performed with stainless steel wire. The results were classified into the following 4 ranks:

- ⊙ no trace of scratching
- insignificant trace of scratching
- △ some trace of scratching
- X obvious trace of scratching

The adhesive property of transparent protective layer 12 to surface 10a to which machine work S and M were applied was evaluated based on the degree of peeling of transparent protective layer 12 that occurred when an adhering tape placed on surface 10a was peeled off. The adhesive property was classified into the following 4 ranks:

- ⊙ no peeling of the transparent protective layer
- insignificant peeling of the transparent protective layer
- △ some peeling of the transparent protective layer
- X obvious peeling of the transparent protective layer

As shown in Table 6, an excellent quality of appearance, fingerprint adhesion resistance, scratch resistance and adhesion property of transparent protective layer 12 was obtained in Examples 29 to 35. Also, whiteness, glossiness and the quality of

appearance was improved when the dilution ratio was selected based on the type of machine works (H, S or M) applied.

In contrast, in Comparative Example 3 where no transparent protective layer 12 was formed, bad fingerprint adhesion resistance and scratch resistance properties resulted. In Comparative Example 4, where transparent protective layer 12 was formed without first applying electropolishing, bad quality of appearance and inferior adhesion properties of transparent protective layer 12 resulted.

The quality of appearance of transparent protective layer 12, Vickers hardness (Hv), fingerprint adhesion resistance, scratch resistance and adhesion properties of transparent protective layer 12 were evaluated with respect to the samples prepared by the same method as described above, except that surface 10a of facing member of watches 10 was prepared using the electrolysis treatment method with a treatment time of 30 seconds. The results are shown in Table 7 below.

Table 7

Example No	Dilution ratio	Viscosity of coating solution (cps)	Thickness of trans-parent protective layer ( $\mu\text{m}$ )	Appearance			Hv	Fingerprint adhesion resistance	Abrasion resistance				Adhesive property of transparent protective layer
				H	S	M			Test 1	Test 2	Test 3	Test 4	
36	10%	500	10.0	A	A	C	600	◎	◎	◎	◎	◎	◎
37	30%	450	5.0	A	A	C	500	◎	◎	◎	◎	◎	◎
38	50%	400	4.0	A	A	B	350	◎	◎	◎	◎	◎	◎
39	70%	300	2.0	A	A	B~A	250	◎	◎	◎	◎	◎	◎
40	80%	250	0.8	A	A	A	180	◎	◎	◎	◎	◎	◎
41	90%	200	1.0	A	A	A	200	◎	◎	◎	◎	◎	◎
42	95%	200	1.0	A	A	A	200	◎	◎	◎	◎	◎	◎~◎
Comparative example 5	Transparent protective layer is not formed.			—	—	—	—	X	△	△	△	X	—
Comparative example	80%	250	2.0	D	D	E	250	◎	◎	◎	◎	◎	X

As shown in Table 7, an excellent quality of appearance, fingerprint adhesion resistance, scratch resistance and adhesion property of transparent protective layer 12 was obtained in Examples 36 to 42. Also, whiteness, glossiness and the quality of appearance was improved when the dilution ratio was selected based on the type of machine works (H, S or M) applied.

In contrast, in Comparative Example 5, where no transparent protective layer 12 was formed, bad fingerprint adhesion resistance and scratch resistance properties resulted. In Comparative Example 6, where a transparent protective layer was formed without first applying electropolishing, bad quality in appearance and inferior adhesion properties of transparent protective layer 12 resulted.

The coating liquid used to form transparent protective layer 12 is not limited to those previously described, and any parameter such as composition of the coating liquid, temperature, dilution ratio, viscosity or methods of coating may be modified. For example, various kinds of coating liquids containing inorganic substances such as aluminum oxide, silicon oxide or water glass can be used.

Transparent protective layer 12 is not limited to inorganic substances but may also be composed of a polymer material (an organic film) such as a rigid resin. Also, the method for forming transparent protective layer 12 is not limited to the coating methods described above but may also be formed using other methods of wet plating or dry plating, for example, evaporation, sputtering, ion plating or CVD.



It is usually preferable to form transparent protective layer 12 within 144 hours after removing the surface adhesion substances for surface 10a. Otherwise, an oxidation film begins to form on surface 10a which may cause a slight color change to surface 10a.

Application of this invention is not limited to coating of approximately the entire surface of facing member of watches 10, the facing case or other ornaments, but transparent protective layer 12 may also be formed on part of surface 10a, or on a plurality of portions of surface 10a, of facing member 10 of watches, facing cases or other ornaments.

When a treatment for forming transparent protective layer 12 is applied by providing a masking on the inner face of facing case 10 of watches, transparent protective layer 12 is preferably not formed on the inner face of facing case 10 of watches. Otherwise, there is a possibility that the peelings from transparent protective layer 12, caused when the rear cover is snap-fixed to the case, will interfere with the watch movements, thus causing the retardation of or halt of the watch movements. This can be prevented by not forming transparent protective layer 12 on the engaging faces between the rear cover and case. Accordingly, the precise positioning of mechanical parts of the watch will not be adversely affected by transparent protective layer 12.

This invention is not limited to forming transparent protective layer 12 on a titanium or titanium alloy substrate, but is also applicable to the formation of transparent protective layer

12 on layers of titanium or titanium alloy that have been formed on a substrate of a different material.

Aside from facing cases of wristwatches, bands or completed watches, this invention is also applicable to other kinds of watches and clocks such as portable watches, table clocks or wall clocks.

Furthermore, the benefits of the present invention are suitable to applications other than clocks and watches, such as eye glass frames, tiepins, cuff links, lighters or their cases, pens, rings, necklaces, bracelets, brooches, pendants, earrings, piercing rings, coronets, ornaments, decorations, decorative goods such as interior products (being more or less decorative) and accessories. The invention can also be used for electronic devices such as electronic watches and clocks, portable phones, pocket bells, calculators, personal computers, word processors, printers, copy machines, cameras, video equipments, televisions, audio equipments, electronic toys and a variety of measuring apparatuses.

This invention is also suitable for various kind of components constructed from titanium or titanium alloys.

Thus, according to the foregoing descriptions, this invention provides several advantages over the prior art methods of surface treating of titanium or titanium alloys.

By using the present invention an excellent scratch resistant and fingerprint adhesion resistant transparent protective layer can be formed on the surface of titanium or titanium alloys. By using a glass coating liquid, a transparent protective layer is

easily formed that is highly rigid and that provides excellent corrosion and abrasion resistance.

By using chemical polishing or electropolishing with an etching solution on the surface of titanium or titanium alloys to remove surface adhesion substances, especially those that cause color change, prior to forming the transparent protective layer, the inherent colors of the titanium or titanium alloys are displayed with a high degree of whiteness and glossiness and with an improved quality of appearance. In this way, ornaments are given a high class appearance, increasing their commercial value.

Also, when chemical polishing with an etching solution is used, the appropriate selection of the composition of the etching solution or other treatment conditions makes it possible to produce a polished white surface without causing any roughening to the surface. A proper selection of the composition of the electrolyte solution, electric current density and other treatment conditions makes it possible to obtain a good surface that is smooth thus improving the degree of whiteness.

Finally, excellent surface quality can be obtained even when machine works such as honing processing, nicking processing or mirror finishing have been applied to the surface of titanium or titanium alloys.

In one aspect, this invention provides a method for surface treatment characterized by forming a transparent protective layer after applying a treatment for removing surface adhesion substances on the surface of titanium or titanium alloys.

In another aspect, this invention provides a method for surface treatment characterized by forming a transparent protective layer after applying a treatment for removing surface adhesion substances on the surface of titanium or titanium alloys subjected to machine works.

This invention enables the prevention of scratches and contaminations in addition to giving a good quality of appearance. The appearance becomes whitish and glossy because a transparent protective layer is formed after removing surface adhesion substances such as oxide layers, thereby an ornament with a high class appearance can be obtained. The transparent protective layer has a high adhesive property and good durability.

It is preferable that the machine work is any one of honing processing, nicking processing or mirror finishing.

Since surface adhesion substances such as an oxide layer are liable to occur when the machine works above are applied, improvements in the quality in appearance are further effected. This effect is also displayed when any one of the machine works above is applied.

The facing case of a watch is produced by assembling facing members of watches such as a case body, rear cover, cover glass and the like, a bezel being provided around the periphery of the cover glass in some watches. At least one of the case body and bezel of the facing members of watches may be produced with pure titanium or titanium alloys. This invention is applicable to a facing member of watches made of titanium or titanium alloys.

Titanium alloys contain titanium as a main component in which one or two or more kind of metals are incorporated. Examples of the metal to be incorporated into Ti are one or two or more kind of metals such as Al, V, Mo, W, Fe, Co, Cr, Cu, Ag, Pt, Pd and Zn, but are not limited thereto. The content of these metals is not especially limited so long as the metals do not alter the intrinsic properties of titanium.

The facing members of the wristwatch can be produced by a press molding, casting, powder metallurgy process, lost wax process and metal injection molding (MIM) using foregoing titanium or titanium alloy as a starting material. An appropriate cutting process is especially applied to the facing member produced by the press molding, if required.

A machine work is applied, if necessary, on the surface of the facing member of watches. Examples of such machine work are a honing processing by blasting fine grains, a nicking processing and a mirror finishing by buff finishing or barrel finishing.

Titanium is a metal so liable to be oxidized that an oxide layer (color change layer) mainly comprising titanium oxide is often formed by a surface oxidation. Formation of this oxide layer becomes evident when the machine works described above are applied. Formation of this oxide layer makes the surface blackish and deteriorates the quality in appearance, therefore it should be avoided as much as possible.

In a preferred embodiment of the invention, the transparent protective layer is a layer containing a glass component.

This construction of the invention enables the forming of a surface with a sufficient amount of hardness having an excellent scratching resistance, protecting contaminations like adhesion of with fingerprints and mechanical damages in a high level.

In a preferred embodiment of the invention, the transparent protective layer is formed by allowing a glass coating liquid to adhere on the surface subjected to the treatment for removing surface adhesion substances, followed by drying.

This construction of the invention enables the easy forming of a transparent protective layer with a high adhesive property of the layer.

In a preferred embodiment of the invention, the glass coating liquid is used after diluting its original liquid. It is especially preferable that the transparent protective layer is formed by allowing the glass coating liquid prepared by diluting its original liquid in a dilution ratio corresponding to the machine works to adhere, followed by drying.

This construction of the invention enables the improvement of the degree of whiteness and glossiness while maintaining a high degree of corrosion resistance, abrasion resistance and scratching resistance.

In a preferred embodiment of the invention, the viscosity of the glass coating liquid is 150 cps (25°C) or more.

This construction of the invention further improves corrosion resistance, abrasion resistance and scratching resistance.

In a preferred embodiment of the invention, drying is carried out twice or more under different drying conditions.

This construction of the invention improves film quality and adhesive property of the transparent protective layer.

In a preferred embodiment of the invention, the treatment for removing surface adhesion substances is a chemical polishing with an etching solution.

This construction of the invention enables one to effectively remove the surface adhesion substances, especially a layer of titanium oxide.

In a preferred embodiment of the invention, the etching solution comprises a mixed solution containing HF, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

This construction of the invention enables one to make the surface white without roughening the surface of Ti or Ti alloys.

In a preferred embodiment of the invention, the etching solution is an aqueous solution containing 1 to 10 vol% of HF, 15 to 40 vol% of HNO<sub>3</sub> and 30 to 60 vol% of H<sub>2</sub>SO<sub>4</sub>.

This construction of the invention makes it possible to constantly produce an ornament having a high quality in appearance with a high productivity.

In a preferred embodiment of the invention, the temperature of the etching solution is 30 to 75°C and the treatment time with the etching solution is 5 to 50 seconds.

This construction of the invention also makes it possible to obtain a better quality in appearance besides improving the productivity.

In a preferred embodiment of the invention, the treatment for removing surface adhesion substances is an electropolishing.

This construction of the invention enables one to effectively remove the surface adhesion substances, especially foreign materials and a layer of titanium oxide.

In a preferred embodiment of the invention, the electrolyte solution used for electropolishing contains  $H_3PO_4$ .

This construction of the invention makes surface properties after the electrolysis treatment especially good.

In a preferred embodiment of the invention, the electropolishing is carried out at an anodic current density of 0.5 to 10 Amps/cm<sup>2</sup>.

This construction of the invention makes it possible to allow electropolishing with a high whiteness and high quality in appearance to be rapidly carried out.

In a preferred embodiment of the invention, the time for the electrolysis treatment is 3 seconds to 2 minutes.

This construction of the invention makes it possible to sufficiently apply a required electropolishing without decreasing the productivity.

In a preferred embodiment of the invention, the treatment for removing surface adhesion substances is a treatment at least containing surface washing.

This construction of the invention enables one to easily remove surface adhesion substances, especially surface contaminants and foreign materials having a weak adhering strength.



In a preferred embodiment of the invention, the surface adhesion substances contain Ti oxide that causes blackening.

This construction of the invention enables one to enhance the degree of whiteness, improving the quality in appearance.

This invention provides an ornament characterized in that a transparent protective layer is formed on the surface of a metallic member comprising titanium or titanium alloys where adhesion substances have been removed.

This invention provides an ornament characterized in that a transparent protective layer is formed on the surface where machine works are applied on the metallic member comprising titanium or titanium alloys from which adhesion substances have been chemically removed.

The constructions of this invention enables one to prevent damages and contaminations, providing an ornament having a high quality in appearance. Because a transparent protective layer is applied after removing surface adhesion substances such as oxide layers, a whitish appearance can be obtained together with glossiness, giving a high class sense.

In a preferred embodiment of the invention, the machine work is any one of honing processing, nicking processing or mirror finishing.

When such machine works are applied, surface adhesion substances such as oxide layers are so liable to occur that the improvement of the quality in appearance becomes more eminent. When any one of the machine works above is applied, the effect described above can be also displayed.

In a preferred embodiment of the invention, the transparent protective layer is a layer containing glass components.

This construction of the invention enables one to form a surface provided with a sufficient amount of hardness, highly preventing contaminations such as adhesion of fingerprints and from being damaged.

In a preferred embodiment of the invention, the thickness of the transparent protective layer is 0.2 to 15  $\mu\text{m}$ .

This construction of the invention enables one to obtain a sufficient amount of protective effect as well as endowing the transparent protective group with a good film quality with few faults.

In a preferred embodiment of the invention, the transparent protective layer has a Vickers hardness of 180 to 700.

This construction of the invention further improves the abrasion resistance and scratching resistance of the transparent protective layer.

In a preferred embodiment of the invention, the ornament is a facing member for watches and clocks.

Since an especially excellent quality in appearance is required in the facing member of watches and clocks, this invention by which the foregoing effects are obtained can be advantageously applied.

In a preferred embodiment of the invention, a case is constructed to contain an electronic device at least a portion of which is decorated with the ornament as described previously.

In a preferred embodiment of the invention, the electronic device is timepiece such as a watch or clock.

It will thus be seen that the objects set forth above, and those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above construction without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

## CLAIMS

### IN THE CLAIMS:

1. A method of treating a surface of a substrate containing titanium, comprising the steps of:  
removing surface adhesion substances from said surface, and  
forming a transparent protective layer on said surface.
2. The method of claim 1 wherein said surface include surface adhesion substances which result from the substrate having been subjected to machine works.
3. The method of claim 1, wherein said transparent layer contains glass.
4. The method of claim 1, wherein the step of forming said transparent protective layer includes adhering a glass coating liquid on said surface from which surface adhesions substances have been removed, and drying said surface.
5. The method of claim 4, wherein said glass coating liquid is dried for about 1 to 20 minutes at a temperature in the range of about 20°C to 250°C.
6. The method of claim 4, including the steps of forming said glass coating liquid by diluting an original liquid with a diluting solvent.
7. The method of claim 1, wherein the step of removing surface adhesions substances includes chemical polishing said surface by immersing said surface in an etching solution.

8. The method of claim 7, wherein said etching solution comprises hydrofluoric acid, nitric acid and sulfuric acid.

9. The method of claim 8, wherein said etching solution is an aqueous solution comprising 1% to 10% volume of hydrofluoric acid, 15% to 40% volume of nitric acid and 30% to 60% volume of sulfuric acid.

10. The method of claim 7, wherein the temperature of said etching solution is in the range of about 30°C to 75°C.

11. The method of claim 7, wherein said surface is immersed in said etching solution for about 5 to 50 seconds.

12. The method of claim 1, wherein the step of removing surface adhesion substances includes electropolishing said surface with an electrolyte solution.

13. The method of claim 12, wherein said electrolyte solution contains phosphoric acid.

14. The method of claim 12, wherein said electropolishing procedure employs an anodic current density in the electrolyte solution of about 0.5 to 10 Amps/cm<sup>2</sup>.

15. The method of claim 12, wherein said electropolishing step is performed for about 3 seconds to 2 minutes.

16. The method of claim 12, wherein the electrolyte solution contains H<sub>3</sub>PO<sub>4</sub> in a concentration in the range of about 8% to 12%.

17. The method of claim 1, wherein said step of removing said first adhesion substances includes washing said surface.

18. The method of claim 1, wherein said surface adhesion substances contain titanium oxides that cause blackening of the surface.

19. The method of claim 2, wherein said machine works is selected from the group consisting of honing processing, nicking processing and mirror finishing.

20. The method of claim 6, wherein the step of forming said glass coating liquid includes selecting dilution ratios corresponding to selected machine works and diluting said original liquid to a dilution ratio corresponding to said machine works applied to said surface.

21. The method of claim 20, wherein said glass coating liquid has a viscosity of 150 cps (25°C) or greater and a dilution ratio in the range of about 30% to 70%.

22. The method of claim 20, wherein said glass coating liquid has a viscosity in the range of about 150 to 400 cps (25°C) and a dilution ratio in the range of about 50% to 98%.

23. The method of claim 4, wherein the step of drying said surface includes drying said surface at least two times under different drying conditions.

24. The method of claim 12, wherein the pH of the electrolyte solution is in the range of about 1.0 to 1.2.

25. An ornament, comprising a transparent protective layer formed over at least a portion of a surface of a metallic member containing titanium which is substantially free of surface adhesion substances.

26. The ornament of claim 25, wherein said transparent protective layer contains glass.

27. The ornament of claim 25, wherein said transparent protective layer has a thickness in the range of 0.2 to 15 microns.

28. The ornament of claim 25, wherein said transparent protective layer has a Vickers hardness in the range of 180 to 700.

29. The ornament of claim 25, wherein said ornament is a facing member for timepieces.

30. The ornament of claim 25, wherein said ornament decorates at least a portion of an electronic device.

31. The ornament of claim 30, wherein said electronic device is a timepiece.

32. An ornament comprising a transparent protective layer formed on a surface of a metallic member containing titanium which had been subjected to machine works and having substantially no surface adhesion substances thereon.

33. The ornament of claim 32, wherein said machine works is selected from the group consisting of honing processing, nicking processing and mirror finishing.

34. The ornament of claim 32, wherein said transparent layer contains glass.

35. The ornament of claim 32, wherein said transparent protector layer has a thickness in the range 0.2 to 15 microns.

36. The ornament of claim 32, wherein said transparent protector layer has a Vickers hardness in the range of 180 to 700.

37. The ornament of claim 32, wherein said ornament is a facing member for a timepieces.

38. The ornament of claim 32, wherein said ornament decorates at least a portion of an electronic device.

39. The ornament of claim 38, wherein said electronic device is a timepiece.



# ABSTRACT OF THE DISCLOSURE

A method for treating surfaces of titanium or titanium alloys which includes the steps of applying a treatment for removing surface adhesion substances from the surface and then forming a transparent protective layer on the surface.

Fig. 1

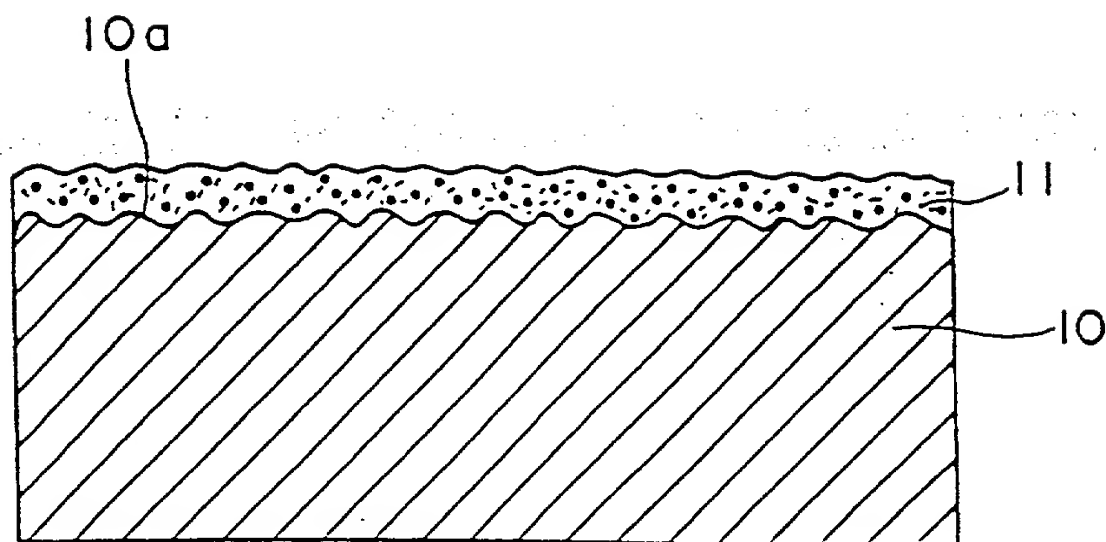


Fig. 2

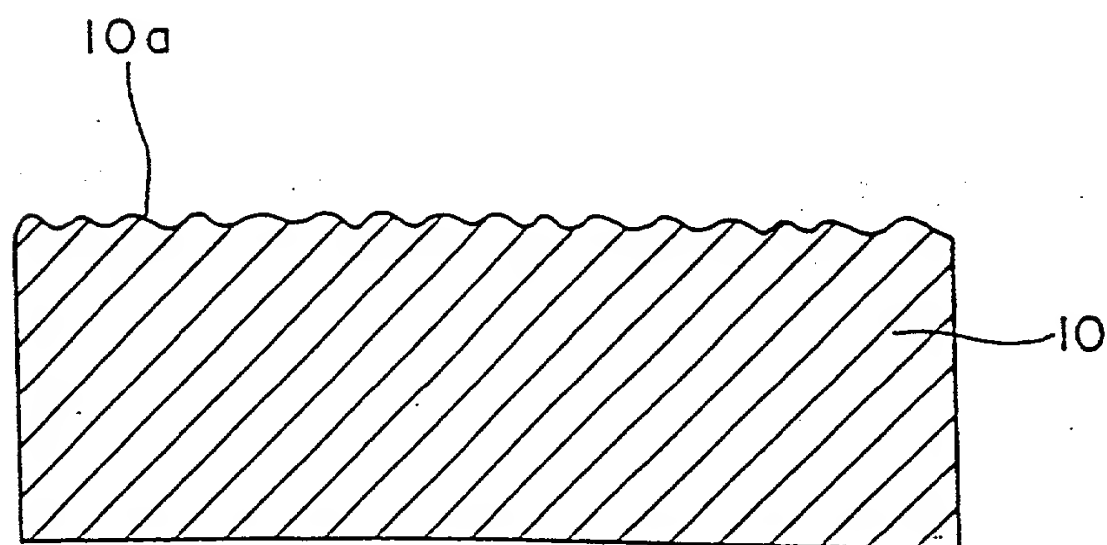


Fig. 3

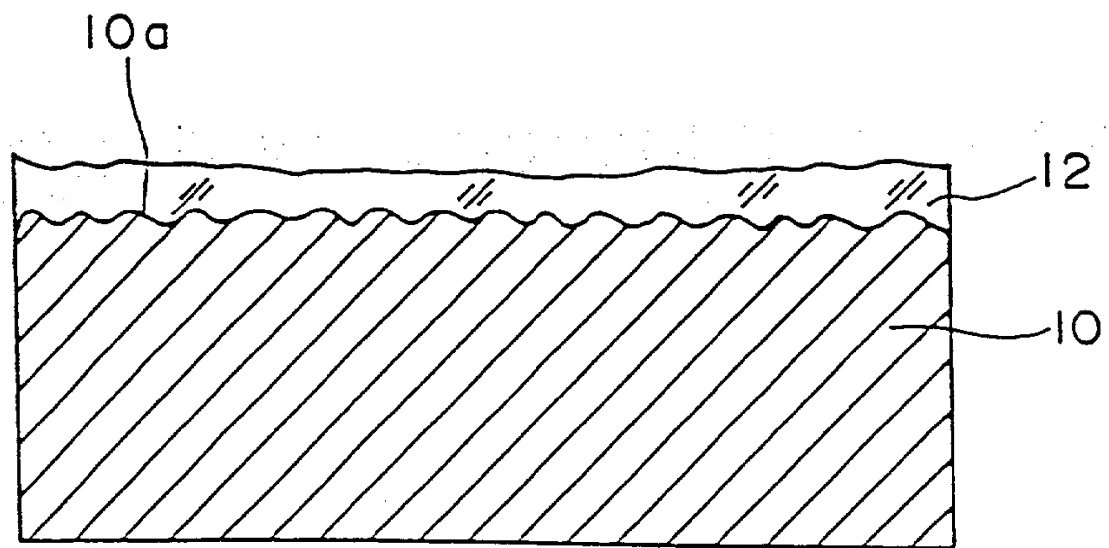


Fig. 4

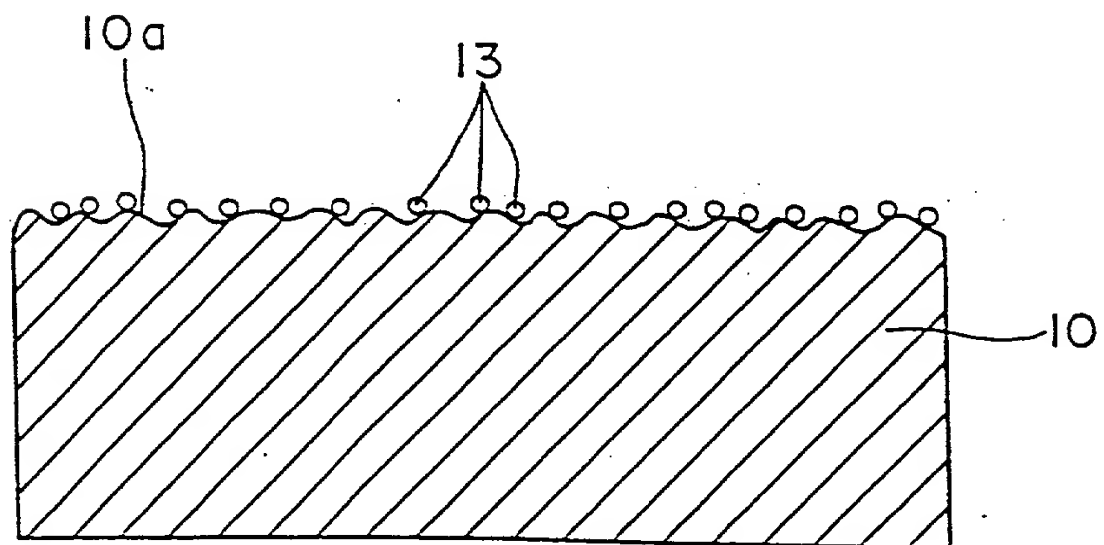


Fig. 5

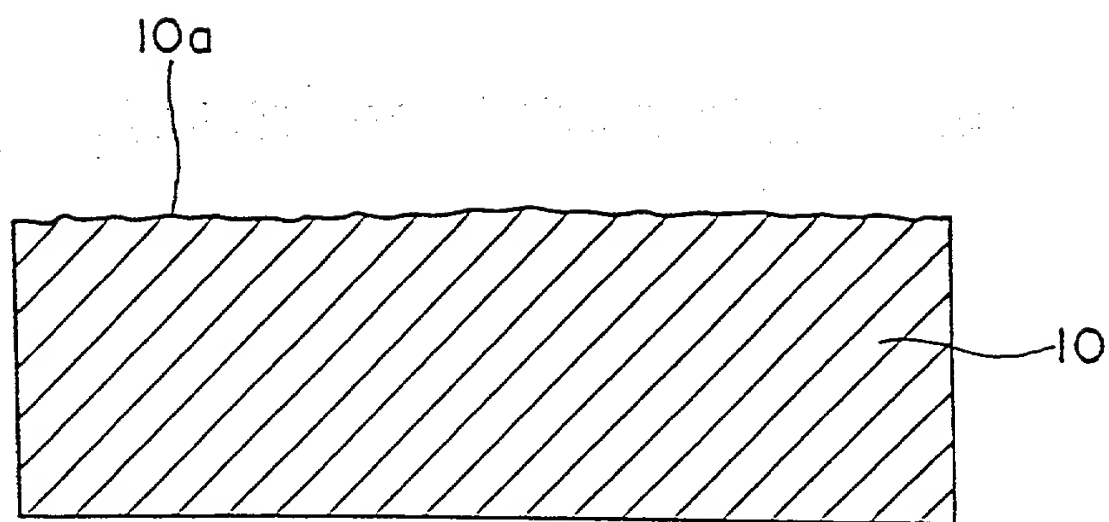
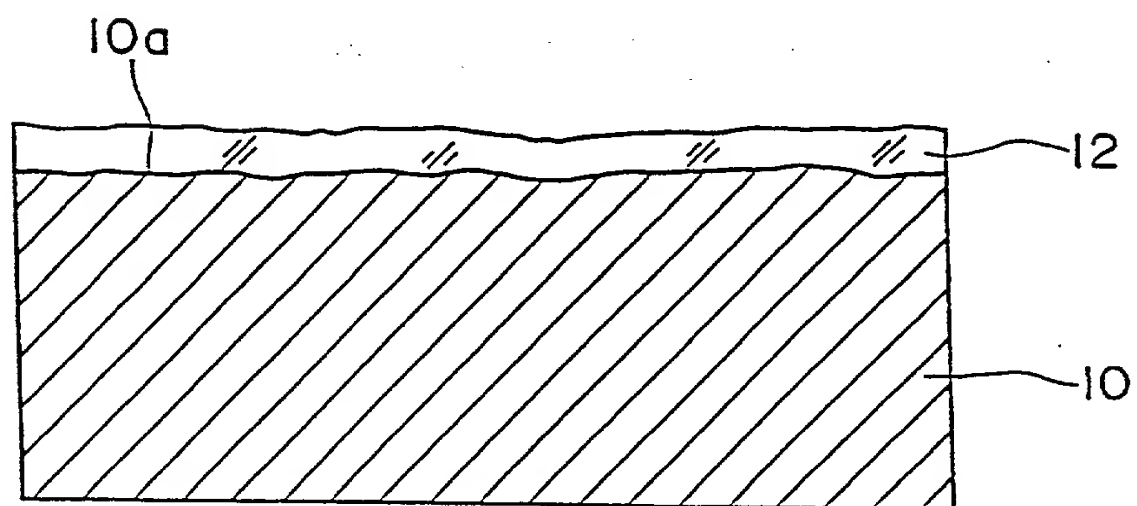


Fig. 6



# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書

### Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣言する：

私の住所、郵便の宛先および国籍は、下欄に氏名に続いて記載したとおりであり、

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

その明細書を  
(該当する方に印を付す)

☐ ここに添付する。

☒ 14/01/98 日に 出願番号

第 09/007,129 号として提出し、

日に補正した。

(該当する場合)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

私は、連邦規則法典第37部第1章第56条 項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

A METHOD FOR SURFACE TREATMENT,

ORNAMENTS AND ELECTRONIC DEVICES

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on January 14, 1998 as

Application Serial No. 09/007,129

and was amended on (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

# Japanese Language Declaration

私は、合衆国法典第35部第119条にもとづく下記の外国特許出願または発明者証出願の外国優先権利益を主張し、さらに優先権の主張に係わる基礎出願の出願日前の出願日を有する外国特許出願または発明者証出願を以下に明記する：

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior foreign applications  
先の外国出願

Priority claimed  
優先権の主張

9-5008	Japan	14 January 1997
(Number)	(Country)	(Day/Month/Year Filed)
(番 号)	(国 名)	(出願の年月日)
9-277839	Japan	9 October 1997
(Number)	(Country)	(Day/Month/Year Filed)
(番 号)	(国 名)	(出願の年月日)
(Number)	(Country)	(Day/Month/Year Filed)
(番 号)	(国 名)	(出願の年月日)

<input checked="" type="checkbox"/>	<input type="checkbox"/>
Yes	No
あり	なし
<input checked="" type="checkbox"/>	<input type="checkbox"/>
Yes	No
あり	なし
<input type="checkbox"/>	<input type="checkbox"/>
Yes	No
あり	なし

私は、合衆国法典第35部第120条にもとづく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第35部第112条第1項に規定の態様で先の合衆国出願に開示されていない限度において、先の出願の出願日と本願の国内出願日またはPCT国際出願日の間に公表された連邦規則法典第37部第1章第56条項に記載の所要の情報を開示すべき義務を有することを認める：

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)  
(出願番号)

(Filing Date)  
(出願日)

(現 況)  
(特許済み、係属中、放棄済み)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)  
(出願番号)

(Filing Date)  
(出願日)

(現 況)  
(特許済み、係属中、放棄済み)

(Status)  
(patented, pending, abandoned)

私は、ここに自己の知識にもとづいて行った陳述がすべて真実であり、自己の有する情報および信ずるところに従って行った陳述が真実であると信じ、さらに故意に虚偽の陳述等を行った場合、合衆国法典第18部第1001条により、罰金もしくは禁錮に処せられるか、またはこれらの刑が併科され、またかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損うことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## Japanese Language Declaration

委任状：私は、下記発明者として、以下の代理人をここに選任し、本願の手続を遂行すること並びにこれに関する一切の行為を特許商標庁に対して行うことを委任する。  
(代理人氏名および登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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Lawrence Rosenthal,	Registration No. 24,377
Steven B. Pokotilow,	Registration No. 26,405
Howard M. Gitten,	Registration No. 32,138
Matthew W. Siegal,	Registration No. 32,941

書類の送付先：

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Direct Telephone Calls to: (name and telephone number)

STROOCK & STROOCK & LAVAN LLP  
(212) 806-5400

唯一のまたは第一の発明者の氏名	Full name of sole or first inventor
	AKIRA UCHIYAMA
同発明者の署名	Inventor's signature
日付	Date
住所	Residence c/o Seiko Epson Corporation 3-5, Owa 3-chome, Suwa-shi, Nagano-ken, Japan
国籍	Citizenship Japan
郵便の宛先	Post Office Address c/o Seiko Epson Corporation 3-5, Owa 3-chome, Suwa-shi, Nagano-ken, Japan
第2の共同発明者の氏名 (該当する場合)	Full name of second joint inventor, if any
同第2発明者の署名	Second Inventor's signature
日付	Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)

# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書及び委任状

### Japanese Language Declaration

#### 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

表面処理方法、装飾品および電子機器

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

☒ 月 日に提出され、14/01/98 として、  
国際出願番号を 09/007,129 とし、  
(該当する場合) 09/007,129 に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されたとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

A METHOD FOR SURFACE TREATMENT,  
ORNAMENTS AND ELECTRONIC DEVICES

the specification of which is attached hereto unless the following box is checked:

☒ was filed on January 14, 1998 ✓  
as United States Application Number or  
PCT International Application Number  
09/007,129 and was amended on  
(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.



# Japanese Language Declaration (日本語宣言書)

私は、米国法典第35編119条(a)-(d)項又は365条(b)項に基づき下記の、米国以外の国の少なくとも一か国を指定している特許協力条約365(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、括弧をマークすることで、示しています。

## Prior Foreign Application(s)

外国での先行出願  
9-5008

(Number)

(番号)

9-277839

(Number)

(番号)

Japan

(Country)

(国名)

Japan

(Country)

(国名)

私は、第35編米国法典119条(e)項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)

(出願番号)

(Filing Date)

(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条(c)に基づき権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

(Application No.)

(出願番号)

(Filing Date)

(出願日)

(Application No.)

(出願番号)

(Filing Date)

(出願日)

私は、私自身の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じることに基づき表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Not Claimed

優先権主張なし

14 January 1997

(Day/Month/Year Filed)

(出願年月日)

9 October 1997

(Day/Month/Year Filed)

(出願年月日)

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)

(出願番号)

(Filing Date)

(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned)

(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)

(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

# Japanese Language Declaration (日本語宣言書)

委任状: 私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。(弁理士、または代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (list name and registration number)

Lawrence Rosenthal - Reg. No. 24,377  
Steven B. Pokotilow - Reg. No. 26,405  
Howard M. Gitten - Reg. No. 32,138  
Matthew W. Siegal - Reg. No. 32,941

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書類送付先

Direct Telephone Calls to: (name and telephone number)

直接電話連絡先: (名前及び電話番号)

唯一または第一発明者名 内山 明		Full name of sole or first inventor Akira Uchiyama	
発明者の署名 内山 明	日付 5/7/98	Inventor's signature Akira Uchiyama	Date 5/2/98
住所 日本国長野県諏訪市大和3丁目3番5号 セイコーエプソン株式会社内		Residence c/o Seiko Epson Corporation 3-5, Owa 3-chome, Suwa-shi, Nagano-ken, Japan	
国籍 日本国		Citizenship Japan	
私書箱 日本国長野県諏訪市大和3丁目3番5号 セイコーエプソン株式会社内		Post Office Address c/o Seiko Epson Corporation 3-5, Owa 3-chome, Suwa-shi, Nagano-ken, Japan	
第二共同発明者			
第二共同発明者		Full name of second joint inventor, if any	
日付		Second inventor's signature	
住所		Date	
国籍		Residence	
私書箱		Citizenship	
		Post Office Address	

(第三以降の共同発明者についても同様に記載し、署名をすること)

(Supply similar information and signature for third and subsequent joint inventors.)